

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 534 189 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **92115062.9**

(51) Int. Cl.⁵: **C08G 64/30**

(22) Date of filing: **03.09.92**

(30) Priority: **24.09.91 JP 243673/91**

(43) Date of publication of application:
31.03.93 Bulletin 93/13

(84) Designated Contracting States:
DE GB NL

(71) Applicant: **mitsubishi petrochemical co., LTD.**

**5-2, 2-chome, Marunouchi
Chiyoda-ku Tokyo 100(JP)**

(72) Inventor: **Yokoyama, Masuzo, c/o Mitsubishi Petroch. Co. Ltd.**

**Yokkaichi Res. Center, 1, Toho-cho
Yokkaichi, Mie(JP)**

Inventor: **Takano, Junji, c/o Mitsubishi Petroch. Co. Ltd.**

**Yokkaichi Res. Center, 1, Toho-cho
Yokkaichi, Mie(JP)**

Inventor: **Takakura, Kazuhide c/o Mitsubishi Petroch. Co.Ltd.**

**Yokkaichi Res. Center, 1, Toho-cho
Yokkaichi, Mie(JP)**

(74) Representative: **Hansen, Bernd, Dr.**

Dipl.-Chem. et al

**Hoffmann, Eitle & Partner Patent- und
Rechtsanwälte Arabellastrasse 4 Postfach**

81 04 20

W-8000 München 81 (DE)

(54) **Method for producing polycarbonate.**

(57) An aromatic polycarbonate of improved color value and high molecular weight is obtained by the addition of phosphorous acid and/or a phosphorous ester to the melt polycondensation reaction medium containing aromatic diol, carbonate diester and a metal-containing compound as ester interchange catalyst during the polycondensation reaction.

EP 0 534 189 A1

BACKGROUND OF THE INVENTION

The present invention relates to a method for producing polycarbonate employing ester interchange.

More specifically, the present invention relates to a method for producing a high molecular weight aromatic polycarbonate with improved color from an aromatic diol and a carbonate diester.

Aromatic polycarbonates have recently been employed as engineering plastics with excellent mechanical properties such as impact strength as well as heat resistance and transparency.

A known method for producing such aromatic polycarbonates, the so-called phosgene process, involves reacting an aromatic diol such as bisphenol with phosgene via interfacial polycondensation. However, a great number of problems have been observed with regard to this process including the requirement of using extremely toxic phosgene, the disposal of a great amount of sodium chloride as a byproduct and health and environmental concerns for the methylene chloride generally employed as the reaction solvent in the process.

The so-called melt process, or non-phosgene process, has also been known for obtaining an aromatic polycarbonate via ester interchange between an aromatic diol and a carbonate diester. The non-phosgene method is regarded as advantageous in that it avoids the various problems of the phosgene process described above and in that the aromatic polycarbonate can be produced more economically.

However, in order to obtain a high molecular weight polycarbonate with excellent mechanical properties in accordance with the non-phosgene method using bisphenol A and diphenyl carbonate, it is required to distill phenol and diphenyl carbonate from a melt of a higher viscosity. Thus, the resulting polycarbonate is generally exposed to vacuum at a temperature of from 250 to 330 °C for a long period of time. The problem arises that the resulting polymer is yellow colored. Employing the non-phosgene method, products of a balanced quality between color value and molecular weight are generally difficult to produce.

With the object of improving the thermal stability and color value of aromatic polycarbonates, a variety of phosphorous compounds have been conventionally used in various methods.

With the object of improving the thermal stability, color value or resistance to hydrolysis of an aromatic polycarbonate during molding and kneading, one known method comprises adding various phosphorous compounds to the polycarbonate during molding and kneading (Japanese Patent Examined Publication Nos. 61-3596 and 62-13775, Japanese Patent Unexamined Publication Nos. 50-51154 and 52-14765, U.S. Patent Nos. 3,305,520 and 3,404,122).

These methods, however, will not prevent the deterioration in color occurring during polymerization since the phosphorous compounds are added after the polymerization of the aromatic polycarbonates.

It is also known to use various phosphorous compounds in the polycondensation reaction for ester interchange. Illustrative of methods of this type are:

- (a) use of a combination of a phosphonite and a hindered phenol in the presence of a quaternary ammonium compound (Japanese Patent Unexamined Publication No. 61-141236);
- (b) use of diphenyl phosphonate in the presence of KBH_4 catalyst (Japanese Patent Unexamined Publication Nos. 62-158719 and 62-169821);
- (c) effecting melt polycondensation with an electron donor phosphorous compound as catalyst (Japanese Patent Unexamined Publication No. 3-54223); and,
- (d) effecting melt polycondensation with ester interchange between an alicyclic diol and a carbonate diester (Japanese Patent Unexamined Publication No. 2-180954).

Employing these methods, however, it is difficult to obtain a high-molecular weight aromatic polycarbonate with excellent color.

SUMMARY OF THE INVENTION

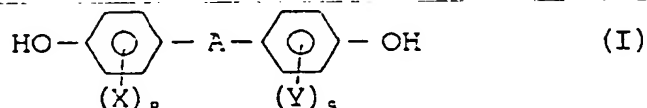
It is an object of the present invention to provide a method for producing a high molecular weight aromatic polycarbonate with improved color by avoiding the problems associated with known melt polycondensation processes involving ester interchange (non-phosgene methods).

The method of the present invention has been achieved after extensive investigation to solve these problems.

That is, the present invention provides a method for producing an aromatic polycarbonate which comprises conducting melt polycondensation of an aromatic diol and a carbonate diester in the presence of a metal-containing compound as ester interchange catalyst and in the presence of phosphorous acid and/or a phosphorous ester to provide the aromatic polycarbonate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The aromatic diol used in the present invention is represented by the following general formula:



wherein A represents a single bond, a substituted or unsubstituted, linear, branched or cyclic divalent hydrocarbon group having up to about 15 carbon atoms, or a divalent group represented by -O-, -S-, -CO-, -SO- or -SO₂-, X and Y, each of which may be identical or different, are hydrogen, halogen or a hydrocarbon group having up to about 6 carbon atoms and p and q independently represent an integer of 0 to 2.

Some representative examples of aromatic diols useful in the practice of the present invention include bisphenols such as bis(4-hydroxydiphenyl) methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3-t-butylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 4,4-bis(4-hydroxyphenyl)heptane, 1,1-bis(4-hydroxyphenyl)cyclohexane, and the like; biphenyls such as 4,4'-dihydroxybiphenyl, 3,3', 5,5'-tetramethyl-4,4'-biphenyl, and the like; bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ketone, and the like. Of these aromatic diols, 2,2-bis(4-hydroxyphenyl)propane is preferred.

Combinations of these aromatic diols can also be used resulting in polycarbonate copolymers. A minor amount of a polyvalent phenol of three or more valences can be copolymerized if a branched aromatic polycarbonate is desired. In order to improve the thermal stability and hydrolytic stability of the desired aromatic polycarbonate, monovalent phenols such as p-t-butylphenol and p-cumylphenol can be used to end-cap the terminal hydroxyl groups.

Some representative examples of carbonate diesters useful in the practice of the present invention include dimethyl carbonate, diphenyl carbonate, ditolyl carbonate, bis(4-chlorophenyl)carbonate, bis(2,4,6-trichlorophenyl)carbonate, and the like.

Generally, these carbonate diester compounds are used in stoichiometric excess relative to the aromatic diol, e.g., in amounts of from about 1.01 to about 1.30 moles, and preferably from about 1.02 to about 1.20 moles, per mole of aromatic diol.

Representative examples of the metal-containing compound used as the ester interchange catalyst herein include known ester interchange catalysts such as the acetates, carbonates, borates, nitrates, oxides, hydroxides, hydrides and alcoholates of such metals as the alkali metals, alkaline earth metals, zinc, cadmium, tin, antimony, manganese, cobalt, nickel, titanium, zirconium, and the like. Preferably, tin-containing ester interchange catalysts and combinations of two or more of such catalysts can be used herein.

Specific examples of ester interchange catalysts which can be used herein include lithium hydride, lithium borohydride, sodium borohydride, potassium borohydride, rubidium borohydride, cesium borohydride, beryllium borohydride, magnesium borohydride, calcium borohydride, strontium borohydride, barium borohydride, aluminum borohydride, titanium borohydride, tin borohydride, germanium borohydride, tetraphenoxy lithium, tetraphenoxy sodium, tetraphenoxy potassium, tetraphenoxy rubidium, tetraphenoxy cesium, sodium thiosulfate, beryllium oxide, magnesium oxide, tin (IV) oxide, dibutyltin oxide, dibutyltin laurate, beryllium hydroxide, magnesium hydroxide, germanium hydroxide, beryllium acetate, magnesium acetate, calcium acetate, tin (IV) acetate, germanium acetate, lithium carbonate, sodium carbonate, potassium carbonate, beryllium carbonate, magnesium carbonate, tin (IV) carbonate, germanium carbonate, tin (IV) nitrate, germanium nitrate, antimony trioxide, bismuth trimethyl carboxylate, and the like.

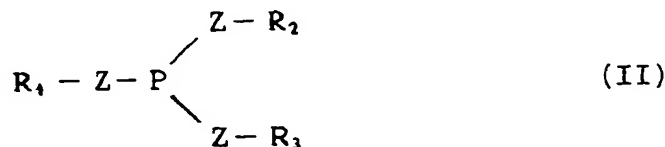
These catalysts may be used at from about 10⁻⁵ to about 10⁻¹ moles, and preferably from about 10⁻⁵ to about 10⁻² moles, per mole of aromatic diol employed in the process.

The present invention is characterized in that an aromatic polycarbonate is produced by using phosphorous acid and/or a phosphorous ester compound under melt polycondensation reaction conditions. Phosphorous compounds which have been employed in the conventional process, for example, phosphines such as tributyl phosphine, triphenyl phosphine, and the like, phosphoric esters such as tributyl phosphate, triphenyl phosphate, triphenyl phosphite, and the like, or phosphorous compounds such as triphenyl phosphine oxide, and the like, cannot achieve the effect of improving the color value of the polycarbonate

product which is the object of the present invention.

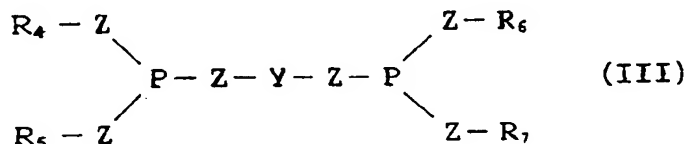
Phosphorous acid which can be used in the present invention can be represented by the chemical formula $P(OH)_3$.

The phosphorous ester compounds which can be used herein can be represented by the following general formulas (II), (III) and (IV):



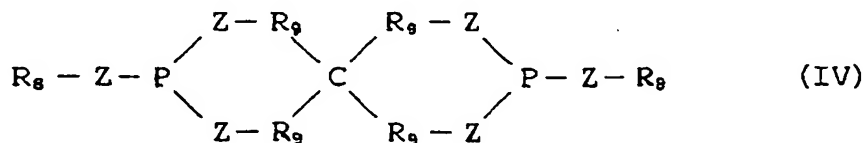
wherein R_1 , R_2 and R_3 independently represent alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 20 carbon atoms and Z represents a single bond or an oxygen atom with at least one of the Zs representing an oxygen atom.

Specific examples of phosphorous esters of formula (II) include triethyl phosphite, tributyl phosphite, tris(2-ethylhexyl) phosphite, tridecyl phosphite, tristearyl phosphite, triphenyl phosphite, tricresyl phosphite, tris(nonylphenyl) phosphite, tris(2,4-di-t-butylphenyl) phosphite, decyl-diphenyl phosphite, phenyl-di-2-ethylhexyl phosphite, phenyl-didecyl phosphite, tris(biphenyl) phosphite, tricyclohexyl phosphite and the like.



wherein R_4 , R_5 , R_6 and R_7 independently represent one of R_1 , R_2 and R_3 as previously defined, Z is as previously defined and Y represents alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 30 carbon atoms.

Specific examples of phosphorous esters of formula (III) include tetraphenyl-4,4'-isopropylidene-diphenol diphosphite, tetratridecyl-4,4'-isopropylidene-diphenol diphosphite, tetratridecyl-4,4'-butylidene bis(3-methyl-6-t-butylphenol) diphosphite, tetrakis(2,4-di-t-butylphenyl-4,4'-biphenylene phosphite, and the like.



wherein R_8 represents an alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 30 carbon atoms, R_9 represents an alkyl having up to about 20 carbon atoms and Z is as previously defined.

Specific examples of phosphorous esters of formula (IV) include bis(stearyl)pentaerythritol diphosphite, bis(2,6-di-6-butylphenyl)pentaerythritol diphosphite, bis(nonylphenyl)pentaerythritol diphosphite, and the like.

Of the various phosphorous esters described above, tributyl phosphite, triphenyl phosphite, bis(stearyl)pentaerythritol diphosphite and bis(2,6-di-t-butylphenyl)pentaerythritol diphosphite are preferred. The phosphorous compound of the present invention can be added to the melt polycondensation reaction medium for ester interchange at any point provided, of course, its intended effect is achieved. Preferably, the phosphorous compound is added during an appropriate reaction stage prior to the final reaction stage.

At the initiation of the reaction, the phosphorous compound can be added simultaneously with the monomers such as the aromatic diol, the carbonate diester and the metal-containing compound ester interchange catalyst which are then mixed together.

In accordance with the present invention, the phosphorous compound is used in at least an amount sufficient to substantially prevent deterioration of the color of the polymer during the melt polycondensation reaction with ester interchange. Amounts of phosphorous compound of from about 10^{-5} to about 10^{-1}

moles, and preferably from about 10^{-4} to about 10^{-2} moles, per mole of aromatic diol compound are generally sufficient to accomplish this. Amounts less than about 10^{-5} moles may not be sufficient to improve the color of the polycarbonate; above about 10^{-1} moles the mechanical strength of the resulting polycarbonate may be reduced. Phosphorous acid or phosphorous ester can be used in an amount of from about 0.03 to about 50 moles; preferably from about 0.1 to about 5 moles, per mole of metal-containing compound used as the ester interchange catalyst.

In accordance with the present invention, melt polycondensation involving ester interchange can be effected in accordance with known melt polycondensation procedures for producing aromatic polycarbonates except that a phosphorous compound is added during the reaction. Such melt polycondensation procedures include heating under atmospheric or reduced pressure while removing byproducts of the ester interchange reaction. The melt polycondensation reaction herein can generally be effected in multiple stages, e.g., two or three stages. The first stage reaction comprises heating the reactants and catalyst at a temperature of 100 to 200 °C in an inert gas atmosphere under atmospheric or reduced pressure. During the first stage reaction, the ester interchange reaction takes place along with the formation of a low molecular weight oligomer having a number average molecular weight of from about 400 to about 1,000. The second stage reaction comprises raising the temperature of the system to about 200 to about 250 °C and continuing the ester interchange reaction while forming a low-molecular weight oligomer with a number average molecular weight of from about 1,000 to about 7,000 and effecting the chain lengthening reaction by bringing about a condition of reduced pressure, for example, of from about 1 to about 20 Torr thereby generating alcohol or phenol which is then removed from the system. In order to increase the chain length of the oligomer further, principally alcohols or phenols and carbonate diesters are removed from the reaction medium in a third stage under a temperature of from about 250 to about 330 °C and a vacuum of from about 0.1 to about 1 Torr or less whereby the high-molecular weight aromatic polycarbonate of this invention is obtained.

The duration of each reaction stage can be adjusted in accordance with the progress of the reaction. In terms of the color value of the polymer obtained, reaction time has little effect when the temperature does not exceed about 200 °C. Generally from about 0.5 to about 5 hours reaction time is suitable at this temperature. At a temperature of from about 200 to about 250 °C, a reaction time of from about 0.1 to about 3 hours is generally suitable. Since prolonged reaction times may have significantly adverse effects on the color tone of the polymer when the reaction temperature exceeds about 250 °C, the reaction time in the final reaction stage is preferably from about 0.1 to about 1 hour depending on the molecular weight of the polycarbonate desired.

The phosphorous compound of the present invention is preferably added during an appropriate reaction stage prior to the final stage of the process. As previously stated, the addition of the phosphorous compound simultaneously with a monomer is one particular embodiment of the present invention.

The aromatic polycarbonate obtained by the method of the present invention has a relatively high molecular weight, e.g., a number average molecular weight (M_n) of from about 10,000 to about 30,000 and a weight average molecular weight (M_w) of from about 20,000 to about 70,000, the M_w/M_n value preferably being from about 2 to about 4.

According to the measurement procedure described hereinbelow, the color value of the polycarbonate obtained by the practice of the present invention is not greater than about 0.1 and is preferably within the range of from about 0.01 to about 0.08.

The method of the present invention will specifically be explained in the working examples which follow. The aromatic polycarbonates of the examples were measured for color value and molecular weight in accordance with the following procedures:

(1) Color

After thermal treatment at 280 °C, the polymer was dissolved in a solvent, methylene chloride, to a concentration of 4 g/100 ml, which was then placed in a cell of a 10 mm optical path. The absorbance at 345 nm was measured by an ultraviolet spectrophotometer. It has been found that the value has a good first-order correlation with the press sheet b value of the polycarbonate at 280 °C, so the color at the absorbance value was evaluated. A smaller numerical value represents better polymer color tone. For example, the color value of the polycarbonate obtained by the phosgene method is in the range of from about 0.030 to about 0.040.

(2) Molecular Weight

Molecular weight is determined as a GPC polystyrene-reduced molecular weight at 35°C using chloroform solvent.

EXAMPLE 1

In a 300 ml capacity SUS reactor equipped with a stirrer and a distillation unit were placed 0.10 moles of bisphenol A, 0.108 moles of diphenyl carbonate, 0.16 mmoles of dibutyltin oxide as a catalyst and 0.27 mmoles (200mg) of bis(stearyl)pentaerythritol diphosphite and left in a molten state at 150°C for 1 hour. After raising the temperature to 200°C, the pressure was gradually decreased to 20 Torr. These conditions were maintained for 1 hour to distill phenol. Subsequently, the pressure was decreased to 0.3 Torr and the temperature raised to 270°C for polycondensation for 30 minutes resulting in the production of about 25g of polymer.

According to GPC, the resulting polymer had a molecular weight of $M_n = 13,800$ and $M_w = 46,300$.

In order to measure the color of the resulting polymer, the ultraviolet absorbance (A_{345}) was measured after thermally treating the polymer in ambient atmosphere at 280°C for 15 minutes. The color value was 0.032.

COMPARATIVE EXAMPLE 1

The same conditions were employed for the synthesis of polycarbonate polymer as in Example 1, *supra*, except that no phosphorous compound was used.

According to GPC, the resulting polymer had a molecular weight of $M_n = 8,200$ and $M_w = 22,700$.

Using the same color measurement procedure as in Example 1, the A_{345} value of the polymer was 0.129.

COMPARATIVE EXAMPLE 2

The following experiment demonstrates that the advantages of the present invention will not be achieved if the phosphorous compound is added after polymerization.

Five grams of the polymer obtained in Comparative Example 1 and the solution of 400mg of the phosphorous compound used in Example 1 dissolved in 300 ml of hexane were mixed together followed by evaporation of hexane at 30 to 35°C in an evaporator to obtain a uniform mixture of the polymer and the phosphorous compound. The mixture was dried at 120°C under reduced pressure followed by the same thermal treatment as in Example 1. The color of the resulting product had an A_{345} value of 0.115.

The results described above show that there will be at most only a slight improvement in the color value of the polymer if the phosphorous compound of the present invention is added in the same proportion to the polymer after completion of polymerization whereas the method of the present invention which requires addition of the phosphorous compound during polymerization results in a dramatic improvement in color and has the further desirable effect of increasing the molecular weight of the polycarbonate product.

EXAMPLES 2 TO 6

Except that the various phosphorous compounds shown in Table 1 were used at 1.0×10^{-3} moles per mole of bisphenol A, the same conditions were employed for the synthesis of polymer as in Example 1. Table 1 sets forth the color values and the molecular weights for the resulting polymers, these values having been determined by the same procedures as in Example 1.

Table 1

Exam. No.	Phosphorous compound	Amount of Phosphorous compound in molar ratio to bisphenol A (mg)	Polymer color tone A_{345}	Molecular weight	
				Mn	Mw
1	bis(stearyl) pentaerythritol diphosphite	2.7×10^{-3} (200)	0.032	13,800	46,300
2	tributyl phosphite	1.0×10^{-3} (26)	0.087	13,000	29,900
3	triphenyl phosphite	1.0×10^{-3} (32)	0.063	9,500	25,500
4	tristearyl phosphite	1.0×10^{-3} (84)	0.047	11,800	28,300
5	bis(2,6-di-t-butylphenyl) pentaerythritol diphosphite	1.0×10^{-3} (61)	0.051	15,100	36,500
6	hydroxy phosphite	1.0×10^{-3} (10)	0.065	11,400	29,800
Comparative Example 1 -----		-----	0.129	8,200	22,700

EXAMPLES 7 TO 9

Except that the amount of the phosphorous compound to be used was modified as set forth in Table 2, the same conditions as in Example 1 were employed for the synthesis of the polymers of these examples. Table 2 sets forth the results as follows:

Table 2

Exam. No.	Amount of phosphorous compound* in molar ratio to bisphenol A (mg)	Polymer color tone A_{345}	Molecular weight	
			Mn	Mw
7	0.68×10^{-3} (50)	0.077	14,600	36,100
8	1.4×10^{-3} (100)	0.066	12,300	34,500
9	5.5×10^{-3} (400)	0.038	11,800	34,200

*bis(stearyl)pentaerythritol diphosphite

EXAMPLE 10

This example examines the effect of the timing of the addition of the phosphorous compound in the method of the present invention.

As in Example 1, the same monomers and catalyst in the same amounts were placed in a reactor and maintained in the molten state at 150°C for one hour. After raising the temperature to 200°C , the pressure was gradually decreased to 20 Torr and maintained under these conditions for one hour to distill phenol. Subsequently, the same amount (200mg) of the phosphorous compound used in Example 1 was added to the reactor. Thereafter, the pressure was decreased to 0.3 Torr and the temperature increased to 270°C for the continuation of the polycondensation reaction to provide the polymer.

The polymer had a molecular weight of $M_n = 11,300$ and $M_w = 30,400$ and a color (A_{345}) of 0.044.

EXAMPLE 11

The same conditions as in Example 1 were employed to synthesize the polymer of this example except that 100mg (0.16 mmoles) of dibutyltin dilaurate ($\text{Bu}_2\text{Sn}(\text{O}_2\text{CC}_{11}\text{H}_{25})_2$) was used as the ester interchange

catalyst. The results are set forth in Table 3.

COMPARATIVE EXAMPLE 3

5 The same conditions as in Example 1 were employed for the synthesis of the polymer of this example except that no phosphorous compound was used. The results are set forth in Table 3.

EXAMPLES 12 TO 14

10 The same conditions as in Example 1 were employed to synthesize the polymers of these examples except that 0.5 mmoles or 0.16 mmoles of lithium hydride (LiH) or 0.16 mmoles of calcium acetate was used as the ester interchange catalyst. The results are set forth in Table 3.

COMPARATIVE EXAMPLES 4 TO 6

15 The same conditions as in Examples 12 to 14 including the types and amounts of the metal-containing compound ester interchange catalysts were employed herein except that no phosphorous compound was used. The results are set forth in Table 3.

20

25

30

35

40

45

50

55

Table 3

	Amount of Phosphorous compound* in molar ratio to bisphenol (A) (mg)	Ester Interchange Catalyst		Polymer color tone A_{415}	Molecular weight	
		type	amount (mmoles)		M_n	M_w
Exam. 11	2.7×10^{-3} (200)	$Bu_2Sn(O_2CC_{11}H_{23})_2$	0.16	0.024	11,300	35,600
Comp. Exam. 3	-----	$Bu_2Sn(O_2CC_{11}H_{23})_2$	0.16	0.110	11,500	33,900
Exam. 12	2.7×10^{-3} (200)	LiH	0.50	0.700	12,500	32,400
Comp. Exam. 7	-----	LiH	0.50	1.65	9,400	20,300
Exam. 13	2.7×10^{-3} (200)	LiH	0.16	0.100	9,000	30,600
Comp. Exam. 5	-----	LiH	0.16	0.500	8,600	24,300
Exam. 14	2.7×10^{-3} (200)	$Ca(O_2CCH_3)_2$	0.16	0.091	9,700	24,500
Comp. Exam. 6	-----	$Ca(O_2CCH_3)_2$	0.16	0.117	10,000	24,900

*) bis(stearyl)pentaerythritol diphosphite

EXAMPLE 15

The same conditions were employed as in Example 1 except that 0.05 moles of bisphenol A and 0.05 moles of bis(4-hydroxyphenyl)methane were used as the aromatic diol compounds so as to provide a copolymer.

The resulting copolymer had a molecular weight of $M_n = 10,500$ and $M_w = 39,500$ and color (A_{345}) of 0.040.

COMPARATIVE EXAMPLE 7

The same conditions as in Example 15 were employed herein except that no phosphorous compound was used. The copolymer had a molecular weight of $M_n = 7,500$ and $M_w = 19,800$ and an A_{345} value of 0.125.

COMPARATIVE EXAMPLES 8 TO 11

These examples show that the advantages of the present invention cannot be achieved with phosphorous compounds that are outside the scope of the invention (e.g., as identified in Table 4 below). These examples employed the same conditions as in Example 1, the results being set forth in Table 4.

Table 4

Comparative Example	Phosphorus compound	Amount of Phosphorous Compound in Molar Ratio to bisphenol A (mg)	Polymer color tone A_{345}	Molecular weight	
				M_n	M_w
8	a) PBu_3	$1.0 \times 10^{-3}(20)$	0.165	13,200	29,300
9	b) $(BuO)_3P=O$	$1.0 \times 10^{-3}(27)$	0.270	7,200	20,800
10	c) $(PhO)_3P=O$	$1.0 \times 10^{-3}(33)$	0.135	15,600	35,200
11	d) $Ph_3P=O$	$1.0 \times 10^{-3}(28)$	0.195	15,700	37,700

a) tributyl phosphite

b) tributyl phosphite

c) triphenyl phosphate

d) triphenyl phosphine oxide

The foregoing examples show that the process of the present invention provides high molecular weight aromatic polycarbonate having excellent color properties.

COMPARATIVE EXAMPLE 12

The following experiment demonstrates that the advantages of the present invention will not be achieved if a combination of a phosphorous compound and an ester interchange catalyst is not used. The same conditions were employed for the synthesis of polycarbonate as in Example 2, *supra*, except that no dibutyltin was used, and an oligomer having a molecular weight of $M_n = 930$ and $M_w = 1830$ was obtained.

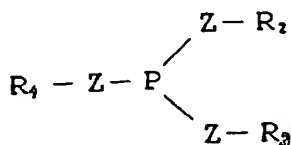
The result described above shows that this example provides no aromatic polycarbonate of practical use.

Claims

1. A method for producing an aromatic polycarbonate which comprises conducting melt polycondensation of an aromatic diol and a carbonate diester in the presence of a metal-containing compound as ester interchange catalyst and in the presence of phosphorous acid and/or a phosphorous ester compound to provide the aromatic polycarbonate.
2. The method according to Claim 1 wherein the ester interchange catalyst is selected from the group consisting of acetate, carbonate, borate, nitrate, oxide, hydroxide, hydride and alcoholate of a metal selected from the group consisting of alkali metal, an alkaline earth metal, zinc, cadmium, tin, antimony, manganese, cobalt, nickel, titanium and zirconium.

3. The method according to Claim 2 wherein the ester interchange catalyst is selected from the group consisting of dibutyltin oxide, dibutyltin laurate, tin oxide, tin acetate, tin carbonate, tin nitrate, lithium hydride, lithium borohydride and calcium acetate.

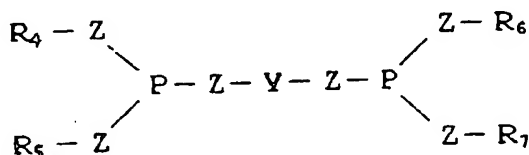
- 5 4. The method according to Claim 1 wherein the phosphorous-ester compound is represented by the
general formula:



wherein R₁, R₂ and R₃ independently represent alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 20 carbon atoms and Z represents a single bond or an oxygen atom with at least one of the Zs representing an oxygen atom.

5. The method according to Claim 4 wherein the phosphorous ester is selected from the group consisting of triethyl phosphite, tributyl phosphite, tris(2-ethylhexyl) phosphite, tridecyl phosphite, tristearyl phosphite, triphenyl phosphite, tricresyl phosphite, tris(nonylphenyl) phosphite, tris(2,4-di-*t*-butylphenyl) phosphite, decyldiphenyl phosphite, phenyl-di-2-ethylhexyl phosphite, phenyl-didecyl phosphite, tris-(*biphenyl*) phosphite and tricyclohexyl phosphite.

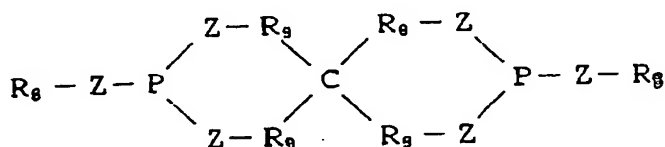
6. The method according to Claim 1 wherein the phosphorous ester is represented by the general formula:



wherein R₄, R₅, R₆ and R₇ independently represent alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 20 carbon atoms, Z represents a single bond or an oxygen atom with at least one of the Zs representing an oxygen atom and Y represents alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 30 carbon atoms.

7. The method according to Claim 6 wherein the phosphorous ester is selected from the group consisting of tetraphenyl-4,4'-isopropylidene-diphenol diposphite, tetratridecyl-4,4'-isopropylidene-diphenol diposphite, tetratridecyl-4,4'-butylidene bis(3-methyl-6-t-butylphenol) diposphite and tetrakis(2,4-di-t-butylphenyl-4,4'-biphenylene phosphite).

8. The method according to Claim 1 wherein the phosphorous ester is represented by the general formula:



wherein R₈ represents alkyl, allyl, cycloalkyl, aralkyl or alkylallyl of up to about 30 carbon atoms, R₉

represents an alkyl of up to about 20 carbon atoms and Z represents a single bond or an oxygen atom with at least one of the Zs representing an oxygen atom.

9. The method according to Claim 8, wherein the phosphorous ester is selected from the group consisting of bis(stearyl)pentaerythritol diphosphite, bis(2,6-di-t-butylphenyl)pentaerythritol diphosphite and bis-(nonylphenyl)pentaerythritol diphosphite.

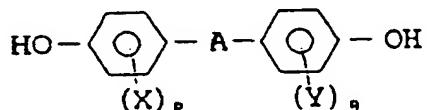
10. The method according to Claim 1 wherein the carbonate diester is used at a level of from about 1.01 to about 1.30 moles per mole of aromatic diol.

11. The method according to Claim 1 wherein the phosphorous acid or phosphorous ester is used at a level of from about 10^{-5} to about 10^{-1} moles per mole of aromatic diol.

12. The method according to Claim 1 wherein the ester interchange catalyst is used at a level of from about 10^{-5} to about 10^{-1} moles per mole of aromatic diol.

13. The method according to Claim 1 wherein the phosphorous acid or phosphorous ester is used at a level of from about 0.03 to about 50 moles per mole of ester interchange catalyst.

14. The method according to claim 1 wherein the aromatic diol is represented by the general formula:



wherein A represents a single bond, a substituted or unsubstituted, linear, branched or cyclic hydrocarbon group of up to about 15 carbon atoms or a divalent group represented by -O-, -S-, -CO-, -SO- or -SO₂-, X and Y, each of which may be identical or different, are hydrogen, halogen or a hydrocarbon group of up to about 6 carbon atoms and p and q independently represent an integer of 0 to 2.

15. The method according to Claim 14 wherein the aromatic diol is selected from the group consisting of bisphenols, biphenyls, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)-ether and bis(4-hydroxyphenyl) ketone.

16. The method according to Claim 15 wherein the bisphenol is selected from the group consisting of bis-(4-hydroxydiphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)-propane, 2,2-bis(4-hydroxy-3-t-butylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane and 4,4-bis(4-hydroxyphenyl)heptane, 1,1-bis(4-hydroxyphenyl)cyclohexane and the biphenyl is selected from the group consisting of 4,4'-dihydroxybiphenyl and 3,3', 5,5'-tetramethyl-4,4'-biphenyl.

17. The method according to Claim 1 wherein the carbonate diester is selected from the group consisting of dimethyl carbonate, diphenyl carbonate, ditolyl carbonate, bis(4-chlorophenyl) carbonate, and bis-(2,4,5-trichlorophenyl) carbonate.

18. The method according to Claim 1 wherein the aromatic polycarbonate has a number average molecular weight (Mn) of from about 10,000 to about 30,000, a weight average molecular weight (Mw) of from about 20,000 to about 70,000 and a value for Mw/Mn of from about 2 to about 4.

19. The method according to Claim 1 wherein the aromatic polycarbonate has a color value (A₃₄₅) of not greater than about 0.1.

20. The method according to Claim 1 wherein the melt polycondensation is carried out in three stages, the first stage comprising heating a reaction medium containing the aromatic diol, the carbonate diester present at a level of from about 1.01 to about 1.30 moles per mole of aromatic diol, the ester interchange catalyst present at a level of from about 10^{-5} to about 10^{-1} moles per mole of aromatic

diol and the phosphorous acid or phosphorous ester present at a level of from about 10^{-5} to about 10^{-1} moles per mole of aromatic diol, at a temperature of from about 100 to about 200 °C in an inert-gas atmosphere under atmospheric pressure or reduced pressure of from about 1 to about 30 kg/cm²g, to produce low molecular weight oligomer,

the second-stage comprising raising the temperature of the reaction medium to about 200 to about 250 °C, reducing its pressure to about 1 to about 20 Torr and removing alcohols or phenols as byproducts from the reaction medium to produce low molecular weight oligomer and chainlengthened product, and

the third-stage comprising increasing the temperature of the reaction medium to about 250 to about 350 °C, reducing its pressure to about 0.1 to less than about 1 Torr, and removing alcohols or phenols and carbonate diesters as byproducts from the reaction medium to produce high molecular weight aromatic polycarbonate.

21. The method according to Claim 20 wherein the aromatic polycarbonate has a number average molecular weight (Mn) of from about 10,000 to about 30,000, a weight average molecular weight (Mw) of from about 20,000 to about 70,000 and a value for Mw/Mn of from about 2 to about 4.

22. The method according to Claim 20 wherein the aromatic polycarbonate has a color value (A_{345}) of not greater than about 0.1.

23. The method according to Claim 20 wherein the first stage is conducted for from about 0.5 to about 5 hours, the second stage is conducted for from about 0.1 to about 3 hours and the third stage is conducted for from about 0.1 to about 1 hour.

24. An aromatic polycarbonate possessing a number average molecular weight (Mn) of from about 10,000 to about 30,000, a weight average molecular weight (Mw) of from about 20,000 to about 70,000, a value for Mw/Mn of from about 2 to about 4 and a color value (A_{345}) of not greater than about 0.1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 5062

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 140 (C-926)(5183) 8 April 1992 & JP-A-40 01 229 (DAICEL CHEM IND LTD) 6 January 1992 * abstract *	1-2,4-5, 10-24	C08G64/30
P,A	--- PATENT ABSTRACTS OF JAPAN vol. 16, no. 140 (C-926)(5183) 8 April 1992 & JP-A-40 01 227 (DAICEL CHEM IN LTD) 6 January 1992 * abstract *	1-2,4-5, 10-24	
P,A	--- PATENT ABSTRACTS OF JAPAN vol. 16, no. 71 (C-913)(5114) 21 February 1992 & JP-A-32 65 625 (DAICEL CHEM IND LTD) 26 November 1991 * abstract *	1-2,8-24	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08G C08K C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 JANUARY 1993	Examiner Kathryn Y.-P. Miao
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

EPO FORM 1503 01.92 (P0401)